

THE CHEMISTRY OF COOKED MEAT FLAVOR

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Except for steak tartare, the delicacy also known as "cannibal steak", civilized man for the most part prefers his meat to have been exposed to some degree of heat. Changes in the meat occur as a result of such exposure; there are changes in tenderness, in moisture content, in color, in size and shape, and most important, from our point of view, changes in flavor. These flavor changes are related to the amount and kind of heat applied. The flavor obtained from exposing a piece of meat to wet heat is obviously not the same as that resulting from subjecting the same piece of meat to dry heat at higher temperatures. Considering the composition of meat, as we shall later on, it appears that the flavor changes are the result of chemical reactions induced by the heat. Therefore, to learn what meat flavor is, it seems advisable to determine the components of the flavor, their precursors and the chemical reactions leading from one to the other.

The flavor of cooked meat is related to the conditions of preparation, and since meat is usually cooked in such a manner as to attain the maximum degree of tenderness, flavor development may be limited. Meat is prepared in either of two ways: by dry heat, as in roasting and broiling, or by moist heat as in stewing or braising. Thus, a piece of meat with a great deal of connective tissue is exposed to moist heat to tenderize it without great regard to flavor development. The meat is exposed to temperatures up to 100°C for long periods of time, and since small pieces are often used, internal and external temperatures are more easily equalized. The flavor developed --taste and aroma--is generally on the more delicate side. Furthermore, the exposure to water results in the leaching of the water-soluble flavor precursors. When meat is exposed to dry heat temperatures in the order of 180 to 190°C are used. The surface undergoes drastic physical and chemical changes. Initially, as the moisture on the surface is boiled away, the flavor developed would be similar to the moist heat-treated meat. However, liquid moves from the interior to replace the surface moisture, carrying with it soluble components of the tissues. As the concentration of these compounds increases, they become involved in chemical reactions resulting in the development of changing spectra of flavor and color. With increasing temperatures, fat melts and covers the entire surface, and the decomposition products formed enter into reactions with the other meat components or contribute their own flavors to the overall flavor.

The flavor of cooking meat is not stable. With increasing temperatures, the flavor develops from bland to desirable, then finally to harsh, acrid unpleasant notes as protein destruction occurs. For example: leg of lamb roasts have a more characteristic flavor at an internal temperature of 65° than at 75°, and on continued cooking the sulfury note is intensified (1).

Evaluation of meat flavor has been carried out either in a subjective manner, to characterize the components of the flavor, or by analytical techniques in an effort to identify the chemicals present in meat aroma. Caul, et al, reported a flavor profile analysis describing meat taste and aroma (Table 1) for beef, veal, pork and lamb broiled by a standard procedure (2). They used such descriptive terms as livery, salivating, and mouth filling. While these characterizations are of great interest, they do not help us with the identification of the chemical factors in flavor. Somewhat more realistic descriptions were given by Crocker (3) who described the aroma of a piece of meat heated at 100°C for 20 minutes as an alkaline odor, smelling like a mixture of amines, including piperidine. In a distillate collected from boiling lean beef, it was possible to identify by odor ammonia, a fishy smelling amine, an indole-like odor, a crackery smelling note like piperidine, and H₂S. After acidifying the distillate acetic and propionic acids were noted. Pork treated the same way had a meaty character similar to beef with superimposed sweetness of taste and volatile fatty acids. There were more basic notes in the aroma including an earthy potato type, and sulfury tones suggestive of chicken. Lamb was more alkaline than beef or pork and had a more marked hexylamine odor. There was a strong caprylic-pelargonic odor characteristic of sheep. Sulfury odor was not conspicuous in lamb. Crocker also claimed that cooking developed the flavor in the meat fiber and not in the juice.

Kramlich and Pearson (4), on the other hand, showed that juice pressed from beef and heated at 93°C developed a cooked meat flavor. It was less unpleasant than the flavor of the uncooked liquid, but both had a strong visceral, animal-like taste.

The increasing utilization of instrumental and micro-analytical techniques for isolation and identification of volatile compounds has led to the characterization of a number of chemicals present in the volatile fraction of meat aroma. Raw beef odor has not been studied extensively, thus only a few components have been identified (5). These are shown in Table 2 with the compounds that have been identified in cooked beef, pork, and lamb aromas. These aromas were developed by heating meat slurry or meat extract at 100°C and thus represent the odor of boiled meat or broth. Components of aroma arising at higher temperatures have not been investigated. The chemicals identified do not appear to be major contributors to aroma or taste; none of them individually is meaty, and no reports have appeared to indicate that mixing these in any way will produce a desirable odor. Either there must be a definite ratio of combining the chemicals to produce a meaty aroma or the responsible components have not yet been identified.

Some of the components in the volatiles from cooked hams have been identified (6) and a comparison made of uncured and cured hams (Table 3). The major differences appear to be in the larger concentrations of hexanal and n-valeraldehyde in uncured hams. The authors indicated that the nitrate cure may interfere with the oxidation of the unsaturated lipids, a source of the two aldehydes. However, there is no explanation for the increased acetaldehyde and propionaldehyde + acetone concentrations found in cured ham. The components identified in the volatiles from dry cured ham are shown in Table 4, but no attempt was made to relate them to the flavor of the ham (7).

An alternative method in studying flavor is to determine the precursor compounds that yield the aroma on heating and by their isolation describe a limited system including the mechanisms of reactions from precursors to desirable volatiles. Since neither the direct study of the volatiles nor the study of the flavor precursors has yielded the information desired, consideration of the composition of meat and possible reactions giving rise to aromas may be of interest. Chemically, meat is an extremely complex substance consisting of a number of classes of compounds (Table 5). Each of these classes contain many individual components. On being heated the compounds react with themselves and with each other and either produce, or have the potential of producing, a very large number of new substances with a variety of aromas. It is from among these that the few volatiles listed in Table 2 have been identified.

Meat is composed primarily of protein, consisting either of chains of amino acids alone or complexed with such things as metals, lipids, carbohydrates or nucleic acids. Although Crocker (3) felt that meaty flavor was developed on heating the protein fibers, the actual importance of protein in flavor is doubtful. It has been implicated, however, as the source of H_2S that has been detected (8). On heat denaturation at about $70^{\circ}C$, the protein chain unfolds exposing hidden -SH groups. Further heating to about 110° results in oxidation of the -SH groups to -S-S- linkages which, incidentally, leads to a decrease in meat tenderness. The H_2S is formed from the -SH groups, beginning at about 80° and increasing exponentially with increasing temperature and time of heating. These -SH groups are part of the structural protein and do not come from the water soluble exponents. The amount of H_2S evolved is a function of the pH of the meat and thus reflects the nutritional and emotional state of the animal. Greater amounts of H_2S are produced at higher pH levels; meat from starved or excited animals with a higher final pH thus maybe expected to yield more H_2S (9). Hydrogen sulfide is an important flavor note in protein products. At low concentrations it blends and rounds out the meaty flavor, but is undesirable at higher concentrations. In addition to H_2S a number of sulfides, disulfides and mercaptans have been identified. The source of these is not known. They could result from the interaction of H_2S , formed as just described, with fractions from other meat components. Mercaptans also are readily oxidized to disulfides.

It is generally accepted now that the flavor precursors are water soluble (10,11) and that it is among these extractives that the aroma components will be found. Batzer, et al (11,12) reported a glyco-protein fraction in their dialyzed extract which yielded meaty aromas on heating, although Wasserman and Grey (13) and Macy, et al (14) reported only free amino acids in their preparations. The place of the amino acids in flavor development is important, possibly occupying a key role. They are involved in the browning reaction which gives rise to both color and odors. Apparently only the free amino acids are involved. The concentration of amino acids in the protein of leg of lamb before and after roasting did not change (15), while the amino acids concentration in meat extracts did decrease after heating for an hour at $100^{\circ}C$ (14) (Table 6). Although the amino acids may react alone by decarboxylation to form amines or by dehydration to yield diketopiperazines, they are generally considered to interact with reducing sugars and compounds having a dicarbonyl structure. Sugars generally found in meat extracts are glucose, fructose, and ribose in the free or phosphorylated form. There

There have been varying reports of the concentrations of these sugars, but whatever the actual values, glucose is present in greatest concentration and ribose in the least. The reaction between sugar and amino acid, known as the Maillard Reaction, may proceed via two pathways--the Amadori rearrangement and the Strecker Degradation (Table 7). The initial reaction is the condensation of the free amino group with reducing group of the sugar to form an N-substituted glycosylamine. In the Amadori Re-arrangement the N-substituted glycosylamine yields an N-substituted L-amino-1-deoxy ketose, which can undergo a number of further reactions to yield colored and odorous components.

Compounds having a dicarbonyl structure may react with amino acids (Table 8). This is the Strecker degradation. An aldehyde with one carbon atom less than its parent amino acid is formed, as well as free CO₂. The amino group is transferred to the original carbonyl compound to form a new aminated compound that may react with another dicarbonyl molecule.

Of the muscle sugars that react with amino acids, the rate of reaction is greatest with ribose, followed by fructose and finally glucose. The rate of reaction is increased by phosphates and other anions.

The aldehydes formed in the Strecker degradation are odorous and the aromas obtained on heating xylose with a number of amino acids are shown in Table 9 (16). However, the aromas seem to be dependent on the temperature of heating and both Hertz and Shellenbarger (17) and El-Ode', et al (18) recorded the odors obtained by heating sugars and amino acids at 100°C and 180°C. Some of the data of El-Ode', et al on heating several amino acids with glucose or fructose are shown in Table 10. There is a difference in the odors reported by the two groups; Hertz and Shellenbarger, for instance, describe the heated glucose and phenylalanine odor as violets or lilac as opposed to the caramel smell reported by El-Ode', et al. The latter also began a study of the various volatiles formed at several pH levels on heating the various sugars and amino acids at 100° and 180°C. More work should be carried out on these lines.

All of the amino acids described in these studies are present in varying concentration in meat extract yet none gives rise to a meaty aroma on heating individually with a sugar. Wood heated a model system containing all the amino acids in the ratios found in beef extract with glucose (19). The taste was likened to that of authentic meat extract, but could be differentiated. Either the amino acid-sugar reaction may not be all-important for the development of the meat aroma, or the proper conditions for aroma development have not been identified yet. In any case, a great deal of importance is always attached to the interaction of amino acids and sugars, but very little attention is paid to the fact that both the sugars and amino acids alone undergo significant reactions on heating. Merritt et al (20) have demonstrated that on pyrolysis, amino acids give rise to a number of major components (Table 11). The yield may vary from 98% toluene from the amino acid tyrosine to cystine which breaks down to 10-12 major and 10-12 minor components. Introduction of functional groups like -OH or -S into the amino acids (serine, threonine, methionine, cysteine and cystine) increases ease of decomposition and they breakdown into more than 20 compounds each.

The sugars on heating undergo caramelization, changing in color from colorless through shades of amber and brown to a black carbonized mass. The odor also changes from sweet through increasing degrees of bitterness and acridness. Hodge, in his excellent review (21), has discussed the formation of pyruvic aldehyde, acetoin, diacetyl, acetic acid, acetaldehyde, reductones, acetol, furaldehyde (from pentose) and hydroxy methyl furaldehyde (from hexose), glyoxals, pyruvic acid, lactic acid, diacetyl, acetol, etc. Cyclic compounds such as maltol and methyl cyclopentenolone, and various furan derivatives have also been found.

The role of fats in flavor is still undecided. On the one hand, there are a number of workers who indicate that fat had little to do with the taste of cooked meat, but might modify the aroma somewhat. On the other hand, others claim that the species characteristic notes are present in the fat (10). We studied the effect of added fat on the ability of a panel to identify veal as the meat species of the added fat (24). Ground veal roasts given to the panel (Table 12) were identified as veal-33%, beef-32%, pork-24% and lamb-11%. When fat tissue was added at 10% of the weight of the meat, beef fat had no effect on the identification. Pork fat raised the identification significantly, to the point where the veal + fat was identified almost as frequently as real pork. However, when the fat was extracted first, according to the method of Folch, et al (25), the rate of identification fell off. Lamb fat added to veal also led to increased identification of veal as lamb, but after extraction of the fat the rate of identification went up and this combination was identified as often as real lamb; thus, it seems that for beef, the fat plays little role in identification; for pork, there seems to be a water soluble factor in the fat that is precursor for pork flavor, and for lamb there does appear to be a factor associated with the fat that is concentrated by the extraction. Hornstein (20,26) found differences in the compositions of the fats of beef, pork and lamb that might account for overall flavor differences. Lamb contained less free fatty acids (0.4%) than beef and pork (3.7 and 5.5%). Oleic, stearic and palmitic acids make up 99% of lamb free fatty acids, but only 80 to 85% of the fatty acids in beef and pork. The higher concentration of unsaturated fatty acids in the latter meats may account for the increased concentration of the more odorous 2-enals and 2,4-dienals which arise from the breakdown of unsaturated fats. Fats in general may be one source of the short chain fatty acids, saturated and unsaturated carbonyl compounds and the methylketones identified in meat flavor to date. Fats may also be the source of some of the carbonyl compounds that react with amino acids in the browning reaction. The field of lipid chemistry is extensive and the role of lipid compounds in other food flavors has been under investigation for a number of years. A more detailed study of the role of fat in meat flavor is indicated.

Unfortunately meat flavors are not always as desirable as they should be. One unpleasant flavor defect in pork is the boar odor. Studies carried out by Pearson and co-workers (27,28) has shown this to be associated with the non-saponifiable fraction of fat. Some of the components identified in both the boar-odor and boar-odor - free fat fraction of pork are shown in Table 13. Both contained carbonyl compounds, Δ -5 sterols, Vitamin A, squalene, lanosterol, cholesterol and 7-keto sterol. Therefore, unless there are significant quantitative differences, none of these compounds are involved in the boar-odor and further study is indicated.

In the short time available, I have tried to cover some of the chemistry involved in the development of cooked meat flavor. Unfortunately, the studies have not yet led to elucidation of the composition of meat flavor. However, the complexities of the problem and the diversity of possibilities are so intriguing that they whet the appetite for the developments that are sure to be reported in the not too distant future.

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TABLE 1. SOME CHARACTERISTICS OF THE ODOR AND TASTE OF COOKED MEATS (2)

	AROMA	TASTE ^k
BEEF	ANIMAL (LIVER) PROTHY ROSE-FILLING SWEET	SERUM PROTHY ANIMAL (LIVER) MOUTH FILLING SALIVATING BOUQUET
VEAL	ANIMAL (LIVER) SWEET	ANIMAL (LIVER) SWEET SOUR
PORK	ANIMAL (SULFIDE) SWEET FATTY	SWEET ANIMAL (CHICKEN) MOUTH COATING SL. SALIVATING DRY
LAMB	ANIMAL (LIVER) FATTY ACID TALLOW SOUR	SOUR (FATTY ACID) ANIMAL (LIVER) TALLOW V. SL. SALIVATING

TABLE 2. VOLATILE COMPONENTS OF RAW AND COOKED MEAT AROMA (5, 29-33)

FORMALDEHYDE	FORMIC	* H ₂ S
* ACETALDEHYDE	ACETIC	MeS
PROPIONAL	PROPIONIC	* Me ₂ S
METHYLPROPIONAL	2-METHYL PROPIONIC	MeS ₂
3-METHYL BUTANAL	BUTYRIC	
* PROPANONE	iso-BUTYRIC	* MeSH
* 2-BUTANONE	—	* EtSH
DIACETYL	* METHANOL	METHYLAMINE
ACETONE	* ETHANOL	
METHYLPROPYL KETONE		* NH ₃
iso-BUTYRALDEHYDE		
iso-VALERALDEHYDE	* ALSO PRESENT IN RAW BEEF VOLATILES	

TABLE 3. VOLATILE COMPONENTS OF CURED AND UNCURED HAM AROMA (6)

<u>CARBONYL</u>	<u>UNCURED HAM</u>	<u>CURED HAM</u>
	<u>% BY WEIGHT</u>	
ACETALDEHYDE	24.8	39.4
PROPRIONALDEHYDE + ACETONE	16.5	54.8
n-BUTYRALDEHYDE	0.8	0.6
ISOVALERALDEHYDE	1.5	2.7
2-METHYLBUTYRALDEHYDE	0.7	1.5
HEXANAL	50.4	0.7
n-VALERALDEHYDE	5.4	0.3

TABLE 4. VOLATILE COMPONENTS OF DRY CURED HAM (7)

FORMALDEHYDE	ACETONE
ACETALDEHYDE	DIACETYL
PROPIONALDEHYDE	FORMIC ACID
iso-BUTYRALDEHYDE	ACETIC ACID
n-VALERALDEHYDE	PROPIONIC ACID
iso-VALERALDEHYDE	BUTYRIC ACID
METHYLETHYLKETONE	iso-CAPROIC ACID

TABLE 5. SOME CLASSES OF COMPOUNDS FOUND IN MEATS

<u>LIPIDS</u>	<u>PROTEINS</u>
NEUTRAL	STRUCTURAL
PHOSPHOLIPIDS	FUNCTIONAL
STEROLS	<u>NUCLEIC ACIDS</u>
<u>CARBOHYDRATES</u>	RIBONUCLEIC ACIDS
FREE	DEOXYRIBONUCLEIC ACID
PHOSPHORYLATED	NUCLEOTIDES
COMPLEX	NUCLEOSIDES
<u>NON-PROTEIN NITROGEN</u>	FREE BASES
AMINO ACIDS	<u>ACIDS</u>
ACETYLCHOLINE	FREE FATTY ACIDS
ANSERINE, CARNOSINE OTHER PEPTIDES	INORGANIC ACIDS
CREATINE; CREATININE	METABOLIC ACIDS
<u>INORGANIC ELEMENTS</u>	<u>VITAMINS</u>

TABLE 6. EFFECT OF HEAT ON THE CONCENTRATION OF SOME AMINO ACIDS IN DIFFUSATES OF MEAT EXTRACTS (14)

	% CHANGE		
	<u>BEEF</u>	<u>PORK</u>	<u>LAMB</u>
TAURINE	-55	-37	-37
ANSERINE & CARNOSINE	-58	-14	-36
ALANINE	-45	-33	-29
GLUTAMIC ACID	-52	-39	-53
GLYCINE	-45	-42	-47
LEUCINE	-38	-40	-45
GLUCOSE	-42	-35	-36
RIBOSE	100	100	100

TABLE 7. PATHWAYS OF THE AMADORI REARRANGEMENT TO PRODUCE BROWN PRODUCTS (22)

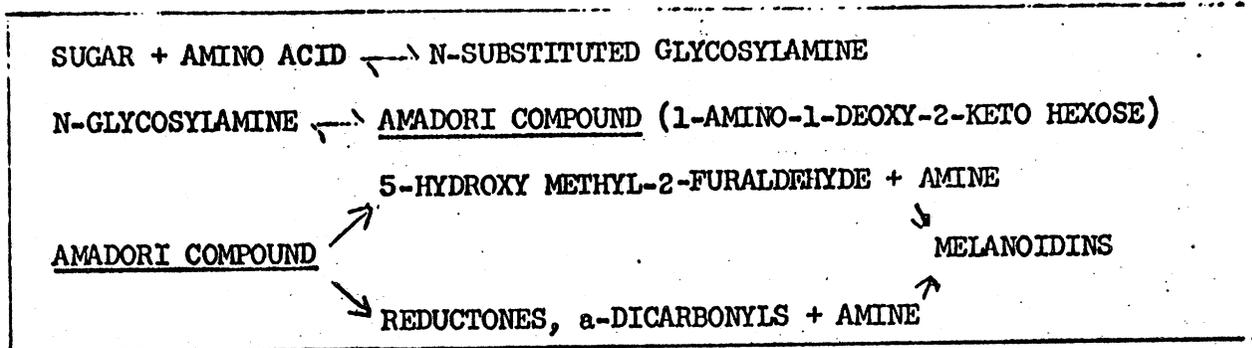


TABLE 8. PATHWAY OF THE STRECKER DEGRADATION TO THE FORMATION OF ODOROUS COMPOUNDS

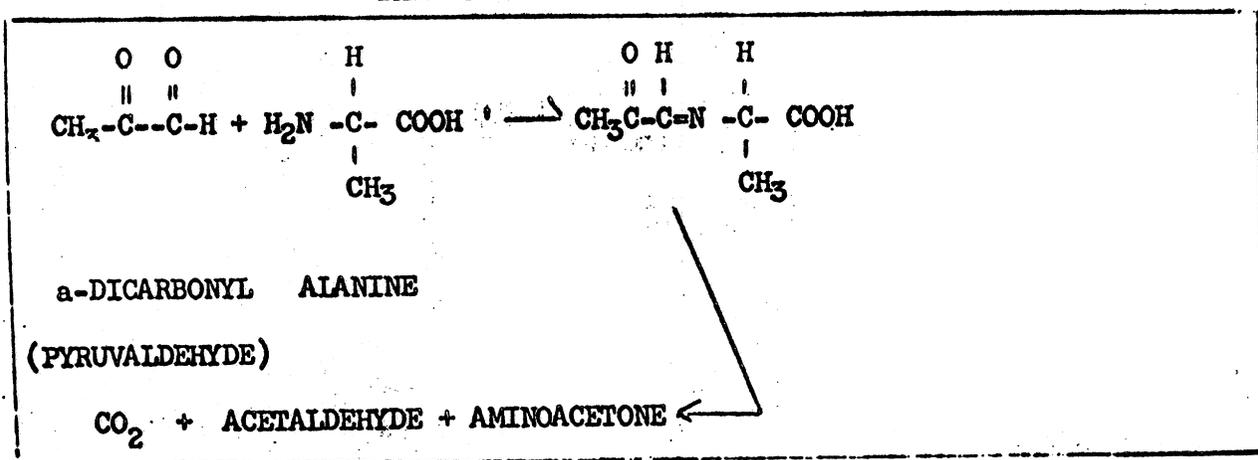


TABLE 9. AROMAS FORMED IN THE REACTION OF SOME AMINO ACIDS WITH XYLOSE (16)

AMINO ACID	AROMA
SERINE	CARAMEL
α -ALANINE	MALT
α -AMINOBUTYRIC ACID	WALNUT
PROLINE	BROWNE FLOUR
VALINE	MALT
LEUCINE	MALT
CYSTEINE	BURNT PROTEIN
CYSTINE	PUFFED RICE
METHIONINE	COOKED CABBAGE
TRYPTOPHAN	BROWNE FAT
PHENYLALANINE	HONEY

TABLE 10. AROMAS FORMED BY THE REACTION OF SOME AMINO ACIDS WITH GLUCOSE AND FRUCTOSE HEATED TO 100° AND 180° AT pH 6.5 (18)

	<u>GLUCOSE</u>		<u>FRUCTOSE</u>	
	100°	180°	100°	180°
<u>GLYCINE</u>	CARAMEL	CARAMEL	CARAMEL	BEEF BROTH
<u>GLUTAMIC</u>	OLD WOOD	CHICKEN TRAY	WEAK	CHICKEN MANURE
<u>LYSINE</u>	BAKED SWEET POTATO	BURNED FRIED POTATO	FRYING BUTTER	FRIED POTATO
<u>METHIONINE</u>	COOKED SWEET POTATO	CABBAGE	CABBAGE	BEAN SOUP
<u>β ALANINE</u>	RANCID CARAMEL	CARAMEL	STINGING	DIRTY DOG

TABLE 11. PRODUCTS PRODUCED FROM THE PYROLYSIS OF SOME AMINO ACIDS (20)

<u>AMINO ACID</u>	<u>MAJOR PYROLYSIS PRODUCT</u>
GLYCINE	ACETONE
ALANINE	ACETALDEHYDE
β-ALANINE	ACETIC ACID
VALINE	2-METHYLPROPANAL
LEUCINE	3-METHYLBUTANAL
iso-LEUCINE	2-METHYLBUTANAL
SERINE	PYRAZINE
THREONINE	2-ETHYLETHYLENEIMINE
TAURINE	THIOPHENE
METHIONINE	METHYLPROPYL SULFIDE
CYSTINE	METHYLTHIOPHENE
PHENYLALANINE	BENZENE
TYROSINE	TOLUENE
PROLINE	PYRROLE

TABLE 12. EFFECT OF ADDED FAT ON THE CORRECT IDENTIFICATION OF VEAL

	<u>% IDENTIFYING CORRECTLY</u>			
	<u>BEEF</u>	<u>LAMB</u>	<u>PORK</u>	<u>VEAL</u>
GROUND MEAT	71.5	78.5	61.0	50.0
VEAL	32.0	11.0	24.0	33.0
VEAL & FAT	40.8	48.4	45.0	30.0
VEAL & EXT. FAT	38.5	69.5	27.0	34.5

TABLE 13. COMPOUNDS FOUND IN BOTH BOAR ODOR-CONTAINING AND ODOR-FREE PORK FAT (27,28)

CARBONYL COMPOUNDS
UNSATURATED COMPOUNDS
Δ-5 STEROLS
VITAMIN A
SQUALENE
LANOSTEROL
CHOLESTEROL
7-KETO STEROL